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INTRODUCTION TO THE SERIES

This series is designed to provide authoritative reviews in the field of modern electroanalytical chemistry defined in its broadest sense. Coverage is comprehensive and critical. Enough space is devoted to each chapter of each volume so that derivations of fundamental equations, detailed descriptions of apparatus and techniques, and complete discussions of important articles can be provided, so that the chapters may be useful without repeated reference to the periodical literature. Chapters vary in length and subject area. Some are reviews of recent developments and applications of well-established techniques, whereas others contain discussion of the background and problems in areas still being investigated extensively and in which many statements may still be tentative. Finally, chapters on techniques generally outside the scope of electroanalytical chemistry, but which can be applied fruitfully to electrochemical problems, are included.

Electroanalytical chemists and others are concerned not only with the application of new and classical techniques to analytical problems, but also with the fundamental theoretical principles upon which these techniques are based. Electroanalytical techniques are proving useful in such diverse fields as electro-organic synthesis, fuel cell studies, and radical ion formation, as well as with such problems as the kinetics and mechanisms of electrode reactions, and the effects of electrode surface phenomena, adsorption, and the electrical double layer on electrode reactions.

It is hoped that the series is proving useful to the specialist and non-specialist alike—that it provides a background and a starting point for graduate students undertaking research in the areas mentioned, and that it also proves valuable to practicing analytical chemists interested in learning about and applying electroanalytical techniques. Furthermore, electrochemists and industrial chemists with problems of electrosynthesis, electroplating, corrosion, and fuel cells, as well as other chemists wishing to apply electrochemical techniques to chemical problems, may find useful material in these volumes.

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CONTENTS OF VOLUME 22

Introduction to the Series iii
Contributors to Volume 22 v
Contents of Other Volumes xiii

LOOKING AT THE METAL/SOLUTION INTERFACE
WITH THE ELECTROCHEMICAL QUARTZ-CRYSTAL
MICROBALANCE: THEORY AND EXPERIMENT
V. Tsionsky, L. Daikhin, M. Urbakh, and E. Gileadi

I. Introduction 2
   A. Is It Really a Microbalance? 3
   B. Applications of the Quartz Crystal Microbalance 4
   C. The Impedance Spectrum of the EQCM 5
   D. Outline of This Chapter 8
II. Theoretical Interpretation of the QCM Response 8
   A. Impedance 8
   B. The Effect of Thin Surface Films 12
   C. The Quartz Crystal Operating in Contact
      with a Liquid 16
   D. Quartz Crystals with Rough Surfaces 26
III. Electrical Double Layer/Electrostatic Adsorption 33
   A. Introduction 33
   B. Some Typical Results 34
   C. The Potential Dependence of the Frequency 36
THE INDIRECT LASER-INDUCED TEMPERATURE JUMP METHOD FOR CHARACTERIZING FAST INTERFACIAL ELECTRON TRANSFER: CONCEPT, APPLICATION, AND RESULTS
Stephen W. Feldberg, Marshall D. Newton, and John F. Smalley

I. Introduction 102
   A. Why Measure Fast Interfacial Electron Transfer Rate Constants? And How? 103
   B. Background 104
   C. The Underlying Principles of the ILIT Method—The Short Version 106
   D. Definition of Terms 108

II. The Evolution of the ILIT Method for the Study of Fast Interfacial Electron Transfer Kinetics 108
   A. The Temperature-Jump Approach for Studies of Homogeneous Kinetics 108
Contents of Volume 22

B. The Temperature-Jump Approach for Studies of Interfacial Kinetics 108

III. Relevant Electron Transfer Theory: Marcus’s Description of Heterogeneous Nonadiabatic Electron Transfer Reactions 112
   A. Chidsey’s Approach 112
   B. Temperature Dependence 116
   C. How Well Does the Butler-Volmer Expression Approximate Marcus’s Formalism? 118

IV. Analysis of the ILIT Response 120
   A. Response of the Open-Circuit Electrode Potential to a Change in the Interfacial Temperature in the Presence of a Perfectly Reversible Redox Couple Attached to the Electrode Surface 121
   B. The Relaxation of the ILIT Response When the Rate of Electron Transfer Is Not Infinitely Fast 126
   C. When Is the ILIT Response Purely Thermal (i.e., Devoid of Kinetic Information)? 126
   D. The Shape of the Ideal ILIT Perturbation 130
   E. Nonidealities of the Shape of the ILIT Perturbation and Response—Extracting the Relaxation Rate Constant, $k_m$ 134
   F. Correlating $k_m$ to Meaningful Physical Parameters 137

V. Experimental Implementation of ILIT 143
   A. The Cell 143
   C. Preparation of Self-Assembled Monolayers 150
   D. The Electronics 151
   E. Potential Problems 152
   F. Energetic and Timing Considerations for Single and Multiple Pulse Experiments 156
   G. Some Suggested Experimental Protocols 160

VI. A Few Examples of Measurements of Interfacial Kinetics 161
   A. Some Typical Transients 161
   B. Determining the Value of $k^o$ 163
   C. Arrhenius Plots and Evaluation of $\Delta H^*$ and $\Delta H_A$ 163
VII. The Potential of the ILIT Approach 166
VIII. Some Thoughts About Future Experiments 166
IX. Glossary of Terms 170
X. Appendix: One-Dimensional Thermal Diffusion into Two Different Phases 173
References 175

ELECTRICALLY CONDUCTING DIAMOND THIN FILMS: ADVANCED ELECTRODE MATERIALS FOR ELECTROCHEMICAL TECHNOLOGIES
Greg M. Swain

I. Introduction 182
II. Diamond Thin Film Deposition, Electrode Architectures, Substrate Materials, and Electrochemical Cells 185
III. Electrical Conductivity of Diamond Electrodes 194
IV. Characterization of Microcrystalline and Nanocrystalline Diamond Thin Film Electrodes 195
V. Basic Electrochemical Properties of Microcrystalline and Nanocrystalline Diamond Thin Film Electrodes 201
VI. Factors Affecting Electron Transfer at Diamond Electrodes 212
VII. Surface Modification of Diamond Materials and Electrodes 216
VIII. Electroanalytical Applications 219
A. Azide Detection 219
B. Trace Metal Ion Analysis 221
C. Nitrite Detection 224
D. NADH Detection 225
E. Uric Acid Detection 225
F. Histamine and Serotonin Detection 226
G. Direct Electron Transfer to Heme Peptide and Peroxidase 227
<table>
<thead>
<tr>
<th>Contents of Volume 22</th>
<th>xi</th>
</tr>
</thead>
<tbody>
<tr>
<td>H. Cytochrome c Analysis</td>
<td>228</td>
</tr>
<tr>
<td>I. Carbamate Pesticide Detection</td>
<td>228</td>
</tr>
<tr>
<td>J. Ferrocene Analysis</td>
<td>229</td>
</tr>
<tr>
<td>K. Aliphatic Polyamine Detection</td>
<td>230</td>
</tr>
<tr>
<td>IX. Electrosynthesis and Electrolytic Water Purification</td>
<td>238</td>
</tr>
<tr>
<td>X. Optically Transparent Electrodes for Spectroelectrochemistry</td>
<td>239</td>
</tr>
<tr>
<td>XI. Advanced Electrocatalyst Support Materials</td>
<td>251</td>
</tr>
<tr>
<td>A. Composite Electrode Fabrication and Characterization</td>
<td>252</td>
</tr>
<tr>
<td>B. Oxygen Reduction Reaction</td>
<td>259</td>
</tr>
<tr>
<td>C. Methanol Oxidation Reaction</td>
<td>264</td>
</tr>
<tr>
<td>XII. Conclusions</td>
<td>267</td>
</tr>
<tr>
<td>References</td>
<td>268</td>
</tr>
<tr>
<td>Author Index</td>
<td>279</td>
</tr>
<tr>
<td>Subject Index</td>
<td>295</td>
</tr>
</tbody>
</table>
CONTENTS OF OTHER VOLUMES

VOLUME 1

AC Polarograph and Related Techniques: Theory and Practice,
Donald E. Smith
Applications of Chronopotentiometry to Problems in Analytical
Chemistry, Donald G. Davis
Photoelectrochemistry and Electroluminescence, Theodore Kuwana
The Electrical Double Layer, Part I: Elements of Double-Layer Theory,
David M. Monhilner

VOLUME 2

Electrochemistry of Aromatic Hydrocarbons and Related Substances,
Michael E. Peover
Stripping Voltammetry, Emrerecht Barendrecht
The Anodic Film on Platinum Electrodes, S. Gilaman
Oscillographic Polarography at Controlled Alternating Current,
Michael Heyrovksy and Karel Micka

VOLUME 3

Application of Controlled-Current Coulometry to Reaction Kinetics,
Jiri Janata and Harry B. Mark, Jr.
Nonaqueous Solvents for Electrochemical Use, Charles K. Mann
Use of the Radioactive-Tracer Method for the Investigation of the
Electric Double-Layer Structure, N. A. Balashova and
V. E. Kazarinov
Digital Simulation: A General Method for Solving Electrochemical
Diffusion-Kinetic Problems, Stephen W. Feldberg
xv

Contents of Other Volumes

VOLUME 4

Sine Wave Methods in the Study of Electrode Processes, Margaretha Sluyters-Rehbach and Jan H. Sluyters
The Theory and Practice of Electrochemistry with Thin Layer Cells, A. T. Hubbard and F. C. Anson
Application of Controlled Potential Coulometry to the Study of Electrode Reactions, Allen J. Bard and K. S. V. Santhanam

VOLUME 5

Hydrated Electrons and Electrochemistry, Geraldine A. Kenney and David C. Walker
The Fundamentals of Metal Deposition, J. A. Harrison and H. R. Thirsk
Chemical Reactions in Polarography, Rolando Guidelli

VOLUME 6

Electrochemistry of Biological Compounds, A. L. Underwood and Robert W. Burnett
Electrode Processes in Solid Electrolyte Systems, Douglas O. Raleigh
The Fundamental Principles of Current Distribution and Mass Transport in Electrochemical Cells, John Newman

VOLUME 7

Spectroelectrochemistry at Optically Transparent Electrodes; I. Electrodes Under Semi-infinite Diffusion Conditions, Theodore Kuwana and Nicholas Winograd
Organometallic Electrochemistry, Michael D. Morris
Faradaic Rectification Method and Its Applications in the Study of Electrode Processes, H. P. Agarwal
Contents of Other Volumes

VOLUME 8

Techniques, Apparatus, and Analytical Applications of Controlled-Potential Coulometry, Jackson E. Harrar
Streaming Maxima in Polarography, Henry H. Bauer
Solute Behavior in Solvents and Melts, A Study by Use of Transfer Activity Coefficients, Denise Bauer and Mylene Breant

VOLUME 9

Chemisorption at Electrodes: Hydrogen and Oxygen on Noble Metals and their Alloys, Ronald Woods
Pulse Radiolysis and Polarography: Electrode Reactions of Short-lived Free Radicals, Armin Henglein

VOLUME 10

Techniques of Electrogenerated Chemiluminescence, Larry R. Faulkner and Allen J. Bard
Electron Spin Resonance and Electrochemistry, Ted M. McKinney

VOLUME 11

Charge Transfer Processes at Semiconductor Electrodes, R. Memming
Methods for Electroanalysis In Vivo, Jiří Koryta, Miroslav Brezina, Jiří Pradáč, and Jarmila Pradáčová
Polarography and Related Electroanalytical Techniques in Pharmacy and Pharmacology, G. J. Patriarche, M. Chateau-Gosselin, J. L. Vandenbalck, and Petr Zuman
Polarography of Antibiotics and Antibacterial Agents, Howard Siegerman
Contents of Other Volumes

VOLUME 12

Flow Electrolysis with Extended-Surface Electrodes, Roman E. Sioda and Kenneth B. Keating
Voltammetric Methods for the Study of Adsorbed Species, Etienne Laviron
Coulostatic Pulse Techniques, Herman P. van Leeuwen

VOLUME 13

Spectroelectrochemistry at Optically Transparent Electrodes, II. Electrodes Under Thin-Layer and Semi-infinite Diffusion Conditions and Indirect Coulometric Iterations, William H. Heineman, Fred M. Hawkridge, and Henry N. Blount
Polynomial Approximation Techniques for Differential Equations in Electrochemical Problems, Stanley Pons
Chemically Modified Electrodes, Royce W. Murray

VOLUME 14

Precision in Linear Sweep and Cyclic Voltammetry, Vernon D. Parker
Conformational Change and Isomerization Associated with Electrode Reactions, Dennis H. Evans and Kathleen M. O’Connell
Square-Wave Voltammetry, Janet Osteryoung and John J. O’Dea
Infrared Vibrational Spectroscopy of the Electron-Solution Interface, John K. Foley, Carol Korzeniewski, John L. Dashbach, and Stanley Pons

VOLUME 15

Electrochemistry of Liquid-Liquid Interfaces, H. H. J. Girault and D. J. Schiffrin
Ellipsometry: Principles and Recent Applications in Electrochemistry, Shimson Gottesfeld
Voltammetry at Ultramicroelectrodes, R. Mark Wightman and David O. Wipf
Contents of Other Volumes

VOLUME 16

Voltammetry Following Nonelectrolytic Preconcentration, Joseph Wang
Hydrodynamic Voltammetry in Continuous-Flow Analysis, Hari
Gunasingham and Bernard Fleet
Electrochemical Aspects of Low-Dimensional Molecular Solids, Michael
D. Ward

VOLUME 17

Applications of the Quartz Crystal Microbalance to Electrochemistry,
Daniel A. Buttry
Optical Second Harmonic Generation as an In Situ Probe of
Electrochemical Interfaces, Geraldine L. Richmond
New Developments in Electrochemical Mass Spectroscopy,
Barbara Bittins-Cattaneo, Eduardo Cattaneo, Peter Königshoven,
and Wolf Vielstich
Carbon Electrodes: Structural Effects on Electron Transfer Kinetics,
Richard L. McCreery

VOLUME 18

Electrochemistry in Micelles, Microemulsions, and Related
Microheterogeneous Fluids, James F. Rusling
Mechanism of Charge Transport in Polymer-Modified Electrodes,
György Inzelt
Scanning Electrochemical Microscopy, Allen J. Bard, Fu-Ren F. Fan,
and Michael V. Mirkin

VOLUME 19

Numerical Simulation of Electroanalytical Experiments: Recent Advances
in Methodology, Bernd Speiser
Electrochemistry of Organized Monolayers of Thiols and Related
Molecules on Electrodes, Harry O. Finklea
Contents of Other Volumes

Electrochemistry of High-\(T_c\) Superconductors, John T. McDevitt, Steven G. Haupt, and Chris E. Jones

VOLUME 20

Voltammetry of Solid Microparticles Immobilized on Electrode Surfaces, Fritz Scholz and Birgit Meyer
Analysis in Highly Concentrated Solutions: Potentiometric, Conductance, Evanescent, Densometric, and Spectroscopic Methodologies, Stuart Licht
Surface Plasmon Resonance Measurements of Ultrathin Organic Films at Electrode Surfaces, Dennis G. Hanken, Claire E. Jordan, Brian L. Frey, and Robert M. Corn
Electrochemistry in Neuronal Microenvironments, Rose A. Clark, Susan E. Zerby, and Andrew G. Ewing

VOLUME 21

Template-Synthesized Nanomaterials in Electrochemistry, Charles R. Martin and David T. Mitchell
Electrochemical Atomic Layer Epitaxy, John L. Stickney
Scanning Tunneling Microscopy Studies of Metal Electrodes, T. P. Moffat
LOOKING AT THE METAL/SOLUTION INTERFACE WITH THE ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE: THEORY AND EXPERIMENT

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I. INTRODUCTION 2
A. Is It Really a Microbalance? 3
B. Applications of the Quartz Crystal Microbalance 4
C. The Impedance Spectrum of the EQCM 5
D. Outline of This Chapter 8

II. THEORETICAL INTERPRETATION OF THE QCM RESPONSE 8
A. Impedance 8
B. The Effect of Thin Surface Films 12
C. The Quartz Crystal Operating in Contact with a Liquid 16
D. Quartz Crystals with Rough Surfaces 26

III. ELECTRICAL DOUBLE LAYER/ELECTROSTATIC ADSORPTION 33
A. Introduction 33
B. Some Typical Results 34
C. The Potential Dependence of the Frequency 36

IV. ADSORPTION STUDIES 43
A. The Adsorption of Organic Substances 43
B. The Adsorption of Inorganic Species 53

V. METAL DEPOSITION 60
A. Deposition on the Same Metal Substrate 60
B. Early Stages of Metal Deposition on a Foreign Substrate 64
I. INTRODUCTION

The literature concerning the quartz crystal microbalance (QCM) and its electrochemical analogue, the electrochemical crystal microbalance (EQCM) is wide and diverse. Many reviews are available in the literature, discussing the fundamental properties of this device and its numerous applications, including its use in electrochemistry [1–5]. In this chapter we concentrate on electrochemical applications, specifically in studies of submonolayer phenomena and the interaction of the vibrating crystal with the electrolyte in contact with it.

A few examples are treated in detail here, and the advantages and limitations of the EQCM as a tool for the study of fundamental phenomena at the metal/solution interface are discussed.

When the quartz crystal microbalance was first introduced in 1959 [6], it represented a major step forward in our ability to weigh matter. Until then, routine measurements allowed an accuracy of 0.1 mg, and highly sensitive measurements could be made with an accuracy limit of 0.3 µg under well-controlled experimental conditions, (see Ref. 7). The QCM extended the sensitivity by two or three orders of magnitude, into the sub-nanogram regime.

Even used in vacuum or in an inert gas atmosphere at ambient pressure, the QCM acts as a balance only under certain conditions, as discussed below. Then the change of mass caused by adsorption or deposition of a substance from the gas phase can be related directly to the change of frequency by the simple equation derived by Sauerbrey [6]:

\[ \Delta f = -C_m \Delta m \]  

(1)
where \( C_m \) is a constant, representing the mass sensitivity, which is related to known properties of quartz and the dimensions of the crystal, and \( \Delta m \) is the added mass density, in units of g/cm\(^2\).

**A. Is It Really a Microbalance?**

Is the quartz crystal microbalance really a *microbalance*? For one thing, it should rightly be called a nano-balance, considering that the sensitivity of modern-day devices is on the order of 1–2 ng/cm\(^2\) and could be pushed further, if necessary. More importantly, calling it a balance implies that the Sauerbrey equation applies strictly, namely that the frequency shift is the sole result of mass loading. It is well known that this is not the case, and the frequency shift observed could more appropriately be expressed by a sum of terms of the form

\[
\Delta f = \Delta f_m + \Delta f_n + \Delta f_P + \Delta f_R + \Delta f_d + \Delta f_T
\]

(2)

where the different terms on the right-hand side (rhs) of this equation represent the effects of mass loading, viscosity and density of the medium in contact with the vibrating crystal, the hydrostatic pressure, the surface roughness, the slippage effect, and the temperature, respectively, and the different contributions can be interdependent. Even this equation does not tell the whole story, certainly not when the device is immersed in a liquid or in gas at high pressure. It does not account for solution occluded between the ridges of a rough surface or in the pores of a porous substrate. The nature of the interaction between the liquid and the surface, the type of roughness, and internal stress or strain could all affect the response of the quartz crystal resonator. These effects become of major importance particularly when small changes of frequency, associated with submonolayer phenomena, are considered. Some of these factors will be discussed in this chapter.

It should be evident from the above arguments that the term quartz crystal microbalance is a misnomer, which could (and indeed has) lead to erroneous interpretation of the results obtained by this useful device. It would be helpful to rename it the *quartz crystal sensor* (QCS), which describes what it really does—it is a sensor that responds to its nearest environment on the nano-scale. However, it may be too late to change the widely used name. The QCM or its analogue in electrochemistry, the EQCM, can each act as a nano-balance under specific conditions, but not in general.
B. Applications of the Quartz Crystal Microbalance

The most common commercial use of the QCM is as a thickness gauge in thin-layer technology. When used to monitor the thickness of a metal film during physical or chemical vapor deposition, it acts very closely as a nano-balance, providing a real-time measurement of the thickness. Indeed, devices sold for this purpose are usually calibrated in units of thickness (having a different scale for each metal, of course), and claim a sensitivity of less than 0.1 nm, which implies a sensitivity of less than a monolayer.

The other common application of the QCM is as a nano-sensor proper, made sensitive to one gas or another by suitable surface treatment. Selecting the suitable coating on the electrodes of the QCM can determine selectivity and enhance sensitivity. It is not our purpose to discuss sensors in the present review. It should only be pointed out that any such sensor would have to be calibrated, since the Sauerbrey equation would not be expected to apply quantitatively.

1. Applications for Gas-Phase Adsorption

The high sensitivity of the QCM should make it an ideal tool for the study of adsorption from the gas phase. We note that the number of sites on the surface of a metal is typically $1.3 \times 10^{15}$/cm², hence a monolayer of a small adsorbate, occupying a single site, would be about 2.2 nmol/cm². A monolayer of water would therefore weigh about 40 ng/cm², while a monolayer of pyridine would weigh 30–60 ng/cm², depending on its orientation on the surface. Comparing these numbers with the sensitivity of 2 ng/cm² shows that adsorption isotherms could be measured in the gas phase employing the QCM. This has not been done properly until relatively recently, mainly because the device was treated as a microbalance, i.e., it was assumed that the Sauerbrey equation could be applied, and several important terms in Eq. (2) were ignored. Obtaining adsorption isotherm one has to change the pressure over a wide range. Therefore, the changes of properties of the surrounding gas cannot be ignored. This shortcoming was overcome by the present authors [8], who developed the supporting gas method. When this method is employed, the overall pressure is kept constant by a large excess of an inert gas, and the frequency shift of the QCM is measured as a function of the partial pressure of the material being investigated. In this manner all terms in Eq. (2), other than $\Delta f_m$, are essentially zero, and the device acts as a true nano-balance. One intriguing result that was obtained using this method came from a comparison of the adsorption of benzene and pyridine on a gold surface. It was found
that a monolayer of pyridine weighs roughly twice as much as a monolayer of benzene. Since the two molecules have almost the same size and molecular weight, it must be concluded that their configuration in the adsorbed state is different. Benzene is probably adsorbed flat on the surface, while pyridine must be adsorbed perpendicular to it, occupying only half as many sites.

Although the nominal resolution of 2 ng/cm² should be enough to study the adsorption isotherm if the monolayer weighs around 30–60 ng/cm², it is somewhat marginal, and an increase of sensitivity of about one order of magnitude would be desirable. Part of this enhancement could be achieved by increasing the roughness factor on the atomic scale, without influencing the roughness on a scale relevant to the resonance frequency (see Sec. VI).

2. Use of QCM in Liquids

It was not initially obvious that the quartz crystal resonator would operate in liquids until this was proven experimentally [9,10]. The term associated with the influence of the viscosity and density of liquid in Eq. (2) can be written [11] as

$$D_f = C_q(\eta \rho)^{1/2}$$

Since the product of $\sqrt{\eta \rho}$ in liquids is about two orders of magnitude higher than in gases at ambient pressure, the crystal is heavily loaded when transferred from the gas phase into a liquid.

Once the door had been opened to its use in liquids, the potential of the QCM for interfacial electrochemistry was obvious, and the EQCM became popular.

When a QCM is placed in contact with a dilute aqueous solution, the frequency should shift to lower values by about 0.7 kHz according to Eq. (3). In practice, a shift of 1.0–2 kHz is observed, depending on the surface roughness. The effect of roughness is also related indirectly to viscosity and density, since the hydrodynamic flow regime at the surface is altered as a result of roughness [12–14]. Roughness is a major issue in the interpretation of the response of the QCM in liquids, and it is discussed in some detail in the following sections.

C. The Impedance Spectrum of the EQCM

In early studies of the QCM and the EQCM, only the resonance frequency was determined and conclusions were drawn based on the shift of
frequency. Unfortunately, in many cases this shift was attributed to mass loading alone, and it was used to calculate the weight added or removed from the surface, disregarding other factors that affect the frequency. In the past decade, more and more laboratories expanded such studies to include measurements of the impedance spectrum of the crystal [15–25]. This provides an additional experimental variable that can obviously yield further information and a deeper understanding of the structure of the interface. For instance, a variation in the resonance width provides unambiguous proof that mechanisms other than mass loading are also involved.

A series of typical admittance spectra are presented here. In Fig. 1a we show a simple case of metal deposition (gold on a gold substrate). The EQCM acts as a true microbalance in this case. The resonance frequency is shifted to lower values with increasing load, but the shape of the spectrum remains unaltered.

In Fig. 1b the effect of viscosity on the admittance spectrum is shown. Here again the resonance frequency is shifted to lower values with increasing viscosity, but this has nothing to do with mass loading. However, the shape of the spectrum is quite different, and the width at half-height (see below) increases dramatically with increasing viscosity and density of the liquid. Line 1 and the inset in this figure show the response of the QCM in H₂ at ambient pressure. The product of viscosity and density is about four orders of magnitude smaller than in any of the liquids. Correspondingly, the width of the resonance is only about 20 Hz, compared to about 2.5 kHz in the liquid corresponding to line 2.

Another aspect of the admittance spectrum is shown in Fig. 1c. Here the same metal deposition was conducted as in Fig. 1a, but the conditions were purposely chosen to produce a very rough surface (by plating at a current density close to the mass-transport limited value). The width of the resonance is increased and the frequency is shifted to lower values with increasing roughness.

We chose rather extreme cases of viscosity and roughness in Fig. 1b and 1c, for the purpose of illustration. The corresponding shift in frequency is very high, in the range of 5–15 kHz, as compared to changes of frequency of 5–40 Hz typically observed in the studies of electrosorption, double layer, upd, and other submonolayer phenomena. The important conclusion is that even very small changes of viscosity and/or surface roughness (produced inadvertently) could lead to a shift of frequency comparable to that expected for such submonolayer phenomena.
FIG. 1. (a) The real part of the admittance versus frequency: during deposition of gold on a gold-covered EQCM at a current density of 20 μA/cm². (c) The same at 500 μA/cm². (b) The response of the QCM immersed in different media: 1, hydrogen, 1 atm; 2, dimethyl ether; 3, water; 4 and 5, 40% and 50% aqueous solutions of sucrose, respectively. (Inset) Admittance for H₂, on an expanded scale. Arrow ηρ shows the increase of product ηρ. (From Ref. 24.)
change of frequency cannot be generally interpreted to be a result of mass loading alone.

D. Outline of This Chapter

This chapter contains theoretical and experimental sections. In the theoretical section we consider different aspects of the behavior of the vibrating resonator: when it was loaded by additional mass, immersed in viscous media, has undergone changes in surface roughness, etc. We discuss the universal perturbation theory of the influence of slightly rough surfaces on the QCM response and consider the special model for strong roughness, noting that a general model does not exist for such surfaces. Special attention was paid to consideration of the influence of slippage on the QCM at the solid/electrolyte interface.

The QCM is now so widely and extensively used that, in the framework of this chapter, it is not possible to review all the available literature. Hence we limited ourselves here to a review of the experimental data and ideas concerning the studies of submonolayer adsorption and interactions taking place at the metal/solution interface. In other words, this review is restricted to the use of the QCM in fundamental electrochemistry. Furthermore, we did not include studies of electrochemical kinetics with the help of the EQCM, which merits a separate review. The problems of the interpretation of the EQCM response caused by changes taking place at the metal/solution interface are obviously of first priority.

We did not present here a full description of the operation of an EQCM. This topic is well described in previous reviews (see Refs. 1,2) and in many articles published in readily accessible electrochemical journals. However, a few aspects of the experiments with the EQCM are covered in the Appendix (Sec. VIII.B).

II. THEORETICAL INTERPRETATION OF THE QCM RESPONSE

A. Impedance

The shear mode resonator consists of a thin disk of AT-cut quartz crystal with electrodes coated on both sides. The application of a voltage between these electrodes results in a shear deformation of the crystal due to its piezoelectric properties. The crystal can be electrically excited into a
number of resonance modes, each corresponding to a unique standing shear wave across the thickness of the crystal. If a quartz resonator operates in contact with an outer medium, the oscillating surface interacts mechanically with the medium and excites motion in it. The mechanical properties of the medium in contact are reflected in the response of the resonator.

The geometry of the system consisting of a quartz crystal in contact with the outer medium is schematically shown in Fig. 2. The $z$-axis is plotted perpendicular to the plane of contact - the plane $z = 0$ coinciding with the unconstrained face of the quartz resonator, and the plane $z = d$ is its constrained face. The thickness of the quartz crystal is $d$.

When an ac voltage is applied between the electrodes, the motion of the AT cut quartz crystal can be described by a system of two coupled differential equations, which constitute the wave equation for elastic displacements, $u(z,t) = u(z,\omega) \exp(i\omega t)$, and the equations that establish

**FIG. 2.** Schematic sketch of the quartz crystal resonator in contact with a liquid. The contacting medium is a thin film rigidly attached to the crystal surface from one side, at $z = d$. The opposite surface of the crystal ($z = 0$) is unconstrained. $d$ is the thickness of the quartz crystal.
the relationship between displacements and the electrostatic potential, \( \varphi(z,t) = \varphi(z,\omega) \exp(i\omega t) \), [26] are

\[
-\omega^2 \rho_u u(z, \omega) = c_{66} \frac{d^2}{dz^2} u(z, \omega) \tag{4}
\]

\[
\varepsilon_{22} \frac{d^2}{dz^2} \varphi(z, \omega) = \varepsilon_{26} \frac{d^2}{dz^2} u(z, \omega) \tag{5}
\]

Here, \( c_{66} = \mu_q + \left( \varepsilon_{26}^2 / \varepsilon_{22} \right) + i \eta_q \); \( \rho_u, \mu_q \) are the density and shear modulus of quartz, \( \varepsilon_{22}, \varepsilon_{26} \) are the dielectric constant, and the piezoelectric stress coefficient of quartz, \( \eta_q \), is its fictitious viscosity, \( \omega = 2\pi f \) is the angular frequency, and \( f \) is the frequency. Equations (4) and (5) are solved under the following boundary conditions:

1. At the plane \( z = 0 \), the potential equals \( \varphi_0 \) and the stress is zero.
2. At the plane \( z = d \), the potential equals \( -\varphi_0 \) and the ratio of the shear stress, \( c_{66} du(z, \omega)/dz \), acting on the contacting medium to the surface velocity, \( iou(d, \omega) \), equals \( -Z_{out} \).

Here \( Z_{out} \) is the mechanical impedance of the medium contacting the quartz surface. Solution of Eqs. (4) and (5) yields the following expression for the admittance of the quartz resonator [27,28]:

\[
Y = i\omega C_0 + Z_m^{-1} \tag{6}
\]

where \( C_0 = \varepsilon_{22}/d \) is the static capacitance and \( Z_m \) is the motional impedance:

\[
Z_m = \frac{1}{i\omega C_0} \left[ \frac{\phi_q}{K_q^2 \tan(\phi_q/2)} - 1 \right] + \frac{\phi_q}{4K_q^2 \omega C_0} \left[ \frac{Z_{out}/Z_q}{iZ_{out}/Z_q} \right] \tag{7}
\]

and \( K_q^2 = \varepsilon_{26}^2 / \varepsilon_{22} c_{66}, \phi_q = k_q d, Z_q = k_q c_{66}/\omega, \) and \( k_q = \omega \sqrt{\rho_u / c_{66}} \) is the wave number of the shear wave in quartz. The first term in Eq. (7) describes the motional resistance of an unloaded quartz resonator. The second term arises from surface loading and includes the properties of the electrode surfaces and the contacting medium through \( Z_{out} \).

In QCM experiments the surface loading is relatively small [27], that is, \( |Z_{out}/Z_q| << 2\tan(\phi_q/2) \). Under these conditions, the shift of the reso-
nant frequency of the quartz-crystal resonator with respect to the resonant frequency of the unloaded quartz crystal, \( f_0 \), can be written as [12, 29]

\[
\Delta \tilde{f} = \Delta f + i \frac{\Gamma}{2} = i \frac{f_0}{\pi} \frac{Z_{\text{out}}}{Z_q} \quad \text{(8)}
\]

It should be noted that the frequency shift \( \Delta \tilde{f} \) can be a complex number, and its imaginary part, \( \Gamma \), reflects the width of the resonance. Equation (8) shows that the complex frequency shift \( \Delta \tilde{f} \) contains the same information as the mechanical impedance \( Z_{\text{out}} \).

The admittance of the quartz resonator can be presented in terms of an electrical equivalent circuit [2–4, 15, 30–36]. The equivalent circuit for the unloaded quartz crystal consists of a motional branch, which reflects the vibration of the quartz, and a static capacitance, which is in parallel with the motional branch. The motional branch includes a resistance, capacitance, and inductance connected in series. The relationships between the electrical elements and the mechanical parameters describing the crystal motion (mass, compliance, and damping coefficient) were considered in Refs. 37–39. When the surface loading is small, \( |Z_{\text{out}}/Z_q| << 2 \tan(\phi_q/2) \), the influence of the contacting medium enters the equivalent circuit through the mechanical impedance connected in series with the motional branch (see Fig. 3). This impedance reflects the properties of the contacting medium. In particular, mass loading and energy dissipation in the medium can be taken into account through inductance and resistance, respectively. The equivalent circuit representation has been used in a number of works to simulate the response of the QCM [14, 15, 38, 40–47].

This approach is similar to that employed in the analysis of electrochemical impedance spectroscopy, and both suffer from the same drawback: It is necessary to prove that the equivalent circuit is indeed equivalent. This may be possible in certain simple situations, for example, the equivalent circuit for a charge-transfer process occurring under purely activation control, on a homogeneous surface, or the impedance of the EQCM on an ideally smooth surface. Unfortunately, these are rather rare cases. In most cases encountered, the response of the interface is much more complex. It is still possible to use the equivalent circuit approach, but one must increase the number of circuit elements to fit the data to the model over a sufficiently large range of frequency. This requires a parameter-fitting procedure involving numerous adjustable parameters, which makes the validity of the model rather dubious. In the case of the EQCM, for...